(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 569 066 A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 93200974.9

(22) Date of filing: 02.04.93

(51) Int. Cl.5: A01N 37/16, //(A01N37/16, 37:02,37:04,25:04)

(30) Priority: 16.04.92 EP 92201093

(43) Date of publication of application: 10.11.93 Bulletin 93/45

(84) Designated Contracting States: CH DE ES FR GB IT LI NL SE

(71) Applicant: UNILEVER N.V.
P.O. Box 760
NL-3000 DK Rotterdam(NL)
(84) CH DE ES FR IT LI NL SE

(71) Applicant: UNILEVER PLC
Unilever House
Blackfriars
P.O. Box 68
London EC4P 4BQ(GB)
(84) GB

(72) Inventor: Benjamins, Peter
Kruiseltlanden 36
NL-7542 HA Enschede(NL)
Inventor: de Boer, Robbert
Sophiastraat 29 1,
NL-7555 JK Hengelo(NL)

(74) Representative: Tan, Bian An, Ir. et al
Unilever N.V.
Patent Division
P.O. Box 137
NL-3130 AC Vlaardingen (NL)

(54) Disinfectant compositions.

(57) There is provided a concentrated disinfectant composition based on peroxy compounds, being a stable suspension which is suitable to provide an aqueous disinfectant composition with a pH in the range of from 2 to 6, said concentrated composition comprising:

(a) 0.1 - 50 % by weight of a solid substantially water-insoluble organic peroxy acid;

(b) 0.1 - 50 % by weight of a water-soluble organic acid; and having a pH in the range of from 2 to 4.

Furthermore, there is provided an aqueous disinfectant composition, which can be prepared by diluting this concentrated composition.

These disinfectants are suitable for disinfecting objects and surfaces at locations where microbial contamination is of major concern, such as in hospitals and the food and drinks industry.

EP 0 569 066 A1

FIELD OF THE INVENTION

The invention relates to disinfectant compositions. More specifically, it relates to either concentrated or aqueous stable disinfectant compositions containing peroxy compounds. The invention is suitable to be used for disinfecting objects and surfaces at locations where microbial contamination is of major concern, such as in hospitals and in the food and beverage industry.

PRIOR ART AND BACKGROUND TO THE INVENTION

It is known that peroxy acids such as 1,12-dodecane dioic peroxy acids can be effectively applied as anti-bacterial agents in pharmaceutical compositions. US-A- 4,804,530 discloses a method for treating anaerobic bacterial infections particularly in the oral cavity, which method comprises contacting the infected tissue with a safe and effective amount of 1,12-dodecane dioic peroxy acid.

It is also known that peroxy acids such as peroxy acetic acid are broad spectrum biocides that have a wide applicability against bacteria and are usable against viruses, moulds and yeasts. According to EP-A-233 731 peroxy acids of mono carboxylic acids having a carbon chain length of 5 to 8 carbon atoms show enhanced activity against a broad spectrum of micro-organisms. Though only moderately soluble in water, these peroxy acids are sufficiently soluble to be used as aqueous solutions at the required disinfectant concentrations. However, aqueous solutions of these peroxy acids have only limited chemical stability due to the fast decomposition of peroxy acid in water.

However, US-A-4,147,720 discloses,that the chemical stability of aqueous suspensions of solid, substantially water-insoluble peroxy acids is considerably higher. US-A-4,417,720 also mentions that this type of aqueous suspensions,especially of aliphatic diperoxydicarboxylic acids, posses good disinfecting properties.

We have found that a solid, substantially water-insoluble organic peroxy acid such as 1,12-diperoxy dodecane dioic acid did show effective killing ability with respect to various bacteria, such as Staphylococcus aureus, Streptococcus faecalis, Proteus mirabilis and Escherichia coli. However, it failed to kill Pseudomonas aeruginosa when acceptable 1,12-diperoxy dodecane dioic acid concentrations were applied.

Accordingly, an object of the present invention is to provide specific peroxy acid compositions which overcome the above shortcomings, more specifically in that they are sufficiently active against Pseudomonas aeruginosa when diluted to accerptable working concentrations. Another object is to provide specific peroxy acid compositions which are sufficiently stable to permit preformulation, optionally in the form of dilutable concentrates, and storage.

EP-A-461,700 discloses an aqueous disinfectant composition comprising a substantially water-insoluble peroxy acid and a sequestering agent, showing enhanced activity against Pseudomonas Aeruginosa and being sufficiently stable to permit preformulation.

We have now found a very suitable alternative disinfectant composition with which the above-mentioned objects can be effectively achieved. We have surprisingly observed that the incorporation of an effective amount of a water-soluble organic acid into a disinfectant composition containing a peroxy acid will result in a composition with a constant and a storage stable biocidal activity, after dilution with water to acceptable working concentrations. This biocidal activity is such that Pseudomonas aeruginosa is effectively killed.

DEFINITION OF THE INVENTION

The present invention provides a concentrated disinfectant composition based on peroxy acid compounds being a stable suspension which is suitable to provide an aqueous disinfectant composition with a pH in the range of from 2 to 6, said concentrated composition comprising:

(a) 0.1 - 50 % by weight of a solid, substantially water-insoluble organic peroxy acid;

(b) 0.1 - 50 % by weight of a water-soluble organic acid; and having a pH in the range of from 2 to 4.

The invention also provides an aqueous disinfectant composition with a pH in the range of from 2 to 6 and prepared by diluting the concentrated disinfectant composition according to the invention to a working concentration of 0.1-5.0% by weight in water. The invention, further, provides a process for disinfecting a surface or an article wherein the aqueous disinfectant composition according to the invention is applied.

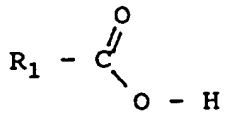
DETAILED DESCRIPTION OF THE INVENTION

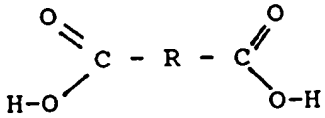
For stability reasons, the concentrates of the aqueous disinfectant compositions according to the present invention have a pH in the range of from 2 to 4. The reason is that organic peroxy acids, particularly

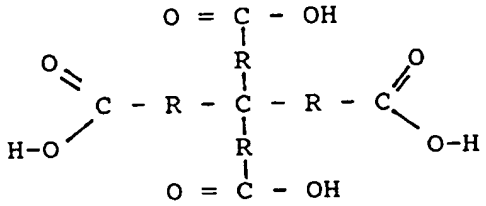
peroxy carboxylic acids, are never 100% stable in a dispersion. They will always slowly decompose. In the pH-range of from 2 to 4, preferably from 3 to 4, most preferably from 3 to 3.5, this decomposition rate is less than 2 % per month at storage temperatures of approximately 20 °C. Above and below this pH-range, the decomposition rate is much larger. When applying 1,12-diperoxy dodecane dioic acid as peroxy acid in the disinfectant composition, it was observed that decomposition of this peroxy acid mainly delivers hydrogen peroxide inside a pH-range of from 3 to 3.5. As a result of this hydrogen peroxide formation the microbicidal activity of the disinfectant decreases.

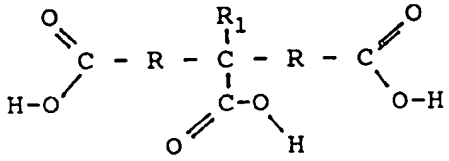
With regard to this decomposition of the peroxy acid to hydrogen peroxide it was unexpectedly found that addition of a water-soluble organic acid counteracts the decrease of the microbicidal activity.

Suitable water-soluble organic acids to be used in disinfectant compositions according to the present invention for maintaining their microbicidal activity, are organic acids with the following structures:

(a) 

(b) 

(c) 

(d) 

wherein R may be independently none, hydrogen or a straight chain or branched C_1-C_8 alkyl group, optionally substituted by an alcohol, sulphate, sulphonate, halogen or amine; and R_1 may be independently hydrogen or a straight chain or branched C_1-C_8 alkyl group, optionally substituted by an alcohol, sulphate, sulphonate, halogen or amine. Preferably citric acid, acetic acid, propionic acid and/or succinic acid are applied as a water-soluble organic acid. More preferably, a combination of citric acid and an acid selected from the group consisting of acetic acid, propionic acid and succinic acid is applied as a water-soluble organic acid. The concentration of the organic acid in the concentrated disinfectant composition is preferably ranging from 0.5 to 20 % by weight.

Preferably, a sequestering agent is present in the disinfectant composition according to the invention. Its concentration is generally lower than 5% by weight, preferably lower than 1 % by weight, as calculated on the weight of the concentrated composition. The function of the sequestering agent is the removal of free metal ions from the concentrated disinfectant composition which ions could negatively influence the stability of the peroxy aid during storage.

Suitable sequestering agents are nitrilotriacetic acid, poly carboxy acid derivatives of amines or poly-amines and various phosphonic acids such as ethylene diamine tetra-(methylene phosphonic acid) or diethylene triamine penta-(methylene phosphonic acid).

Preferably, the solid, substantially water-insoluble organic peroxy acid is a peroxycarboxylic acid derived from a dicarboxylic acid containing 8 to 13 carbon atoms, which dicarboxylic acid is most preferably 1,12-diperoxy dodecane dioic acid. Methods for preparing such organic acids are known in the art.

The disinfectant compositions according to the present invention may further contain any conventional surfactant provided that it contributes to emulsifying the substantially water-insoluble organic peroxy acids. The concentration of this surfactant material is generally in the range from 0 to 50% by weight, but a maximum concentration of 20% is usually preferred. Suitable surfactants may be anionic surfactants, such as alkyl aryl sulfonates, alkyl sulfates and alkyl sulfonates, nonionic surfactants, such as ethylene oxide and/or propylene oxide condensation products with alcohols or alkylphenol, or mixtures thereof. The most preferred surfactant is sodium alkyl benzene sulfonate.

The pH of aqueous disinfectant compositions according to the present invention lies generally in the range of from 2 to 6, preferably from 3 to 5.
For obtaining a constant and storage- stable biocidal activity the pH of the concentrates of these aqueous compositions is desirably in the range of from 3 to 3.5.

Microbicidal activity

It is an essential feature of the disinfectant composition of the invention that the incorporation of a water-soluble organic acid into a disinfectant containing a peroxy acid should bring about an improvement of the microbicidal activity. The microbicidal activity of various disinfectant compositions of the invention on Pseudomonas aeruginosa is assessed using the European Suspension Test (EST), as described in RIVM report nr 357901001 (Appendix 1), 1981. A liquid base composition containing 1,12-diperoxy dodecane dioic acid as peroxy acid, is formulated and subsequently at least one water-soluble organic acid is mixed with this base formulation. Thereafter, the pH of the resulting composition is adjusted to a value of 3.3 (±0.2) with sulphuric acid and finally water is added up to 100 parts (of the full formulation).

The various formulations are contacted with Pseudomonas aeruginosa during 5 minutes at a dilution in the range from 0.1 to 3% wt in water in the presence of 0.03% or 0.3% Bovine Serum Albumin (BSA) and the microbicidal activity is measured as the Logarithmic Decimal Reduction (LDR) of the micro-organism as described for the EST. For the purpose of comparison, a formulation having essentially the same composition as the formulations of the invention but with (more of) an inorganic salt such as sodium sulphate should be used.

The invention will be further illustrated by the following non-limiting examples wherein parts and percentages are by weight.
In these examples the following abbreviations are used:

Dobanoic acid 103	- Dodecylbenzene sulphonic acid (ex Shell)
Marlipal	- C13 Ethoxylated fatty alcohol (90%) with 10 ethylene oxide groups (ex Hüls)
Sodium sulphate	- Sodium sulphate 0 aq. (ex Visser)
Citric acid	- Citric acid 1 aq.
DPDA	- 1,12-diperoxy dodecane dioic acid, 27% active (ex AKZO)

Examples A, 1-4

For the purpose of comparison, the following reference disinfectant composition was formulated.

Constituent	parts
water	60.50
Dobanoic acid 103	7.00
Marlipal	3.33
Sodium sulphate	7.60
DPDA	18.52
Minor ingredients	0.05

The microbicidal activity of this reference composition with respect to Pseudomonas aeruginosa was tested in the presence of 0.03% BSA and at a dilution of this composition of 0.75% wt in water. As a result, an LDR-value of 0.03 was obtained.

Several disinfectant compositions of the invention were formulated by replacing part of the sodium sulphate in the above-described reference composition with a water-soluble organic acid selected from citric acid, acetic acid, propionic acid, and succinic acid. Their microbicidal activity on Pseudomonas aeruginosa at a dilution of 0.75% wt in water and in the presence of 0.03% BSA was tested. In Table 1, the water-soluble organic acids contained in these compositions, their concentration and the LDR-values of their microbicidal activity are listed.

TABLE 1

Example nr.	Type of organic acid	Concentration of organic acid (parts)	LDR-value
1	citric acid	5.5	1.14
2	acetic acid	3.0	1.06
3	propionic acid	3.0	0.57
4	succinic acid	3.0	0.67

It can be seen that the compositions of the invention have a considerably higher microbicidal activity than the reference formulation.

Examples 5-7

Disinfectant formulations containing 2 types of water-soluble organic acid were prepared by adding to the formulation of example 1 another water-soluble organic acid. The microbicidal activity of the resulting disinfectant compositions on Pseudomonas aeruginosa in the presence of 0.03% BSA and at a dilution of 0.75% wt in water was tested.
Table 2 shows the types of additional water-soluble organic acid, their concentration and the LDR-values of the compositions tested.

TABLE 2

Example nr.	Type of additional organic acid	Concentration of additional organic acid (parts)	LDR-value
5	acetic acid	3.0	4.21
6	propionic acid	3.0	3.37
7	succinic acid	3.0	2.37

It can be concluded that disinfectant compositions containing two types of water-soluble organic acids of which one is citric acid, show an increased microbicidal activity as compared to compositions containing only one type of water-soluble organic acid.

Examples 8-11

These examples were carried out in order to find out if the observed major improvement of the microbicidal activity found with the formulations of Examples 5-7 also takes place at higher protein pollutions. For that purpose, the microbicidal activity of the compositions of Examples 1, 5-7 on Pseudomonas aeruginosa was tested in the presence of 0.3% BSA and at a dilution of 1.50% wt in water. Table 3 shows the types of additional water-soluble organic acid - if present-, their concentration and the LDR-values of the compositions tested.

TABLE 3

Example value nr.	Type of additional organic acid	Concentration of additional organic acid (parts)	LDR-
8	-	-	< 5.0
9	acetic acid	3.0	≥ 7.3
10	propionic acid	3.0	≥ 7.3
11	succinic acid	3.0	≥ 7.3

It can be seen that also at a protein concentration of 0.3% BSA (which is 10 times as high as the BSA-level used for Examples 1,5-7) disinfectant compositions containing citric acid and another preferred water-soluble organic acid show a higher microbicidal activity as compared to compositions containing only citric acid.

Example 12

This Example was carried out in order to find out if the improvement of the microbicidal activity found with the formulations of Examples 5-11 can also be found after storage of the formulations during a more or less prolonged period of time.

Starting with the above-shown reference composition, a disinfectant composition according to the present invention was prepared by replacing 6 parts of the sodium sulphate present in the reference composition by 3 parts citric acid and 3 parts acetic acid. Subsequently, the microbicidal activities of both the reference disinfectant composition and the composition according to the invention including the organic acids on Pseudomonas aeruginosa were measured at a dilution of 0.75 %wt and 1.5 %wt in water, both directly after preparing these compositions and after storage thereof at ambient temperature in closed containers during a varying number of weeks.

This microbicidal activity was tested in the presence of 0.03% BSA. Table 4 shows the results found, in terms of the LDR-values of the compositions tested after varying periods of storage.

TABLE 4

Weeks after preparation of the compositions	LDR of the reference composition at a dilution of		LDR of the composition of the invention at a dilution of	
	0.75	1.5	0.75	1.5
0	0.0	0.2	4.6	> 7.9
1	0.1	0.5	5.1	> 8.2
2	0.4	0.1	3.6	5.4
4	0.1	0.2	2.3	> 8.2
7	-	0.0	-	7.9

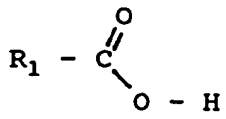
It can be seen that at a dilution of 0.75 %wt in water the improved microbicidal activity of the disinfectant composition according to the invention slowly decreases with storage time. However, a significant LDR-value of 2.3 could still be measured after storage during 4 weeks.

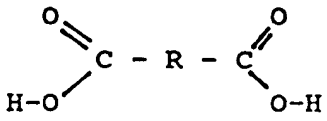
Furthermore, it can be noticed that when tested at a dilution of 1.5 %wt in water the microbicidal activity of the composition of the invention is not even reduced after a storage time of 7 weeks as compared to the activity found directly after preparing the composition.

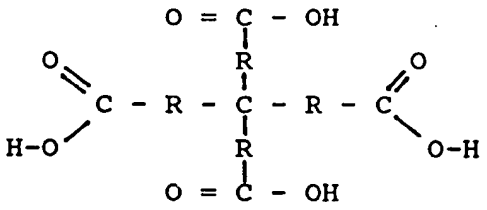
Claims

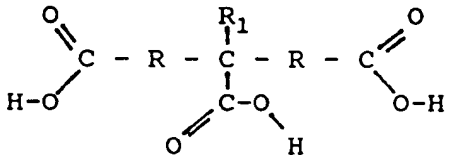
1. A concentrated disinfectant composition based on peroxy compounds, being a stable suspension which is suitable to provide an aqueous disinfectant composition with a pH in the range of from 2 to 6, said concentrated composition comprising:
   (a) 0.1 - 50 % by weight of a solid, substantially water-insoluble organic peroxy acid;
   (b) 0.1 - 50 % by weight of a water-soluble organic acid; and having a pH in the range of from 2 to 4.

2. Composition according to claim 1, wherein the water-soluble organic acid is selected from the group consisting of organic acids with the following structures:

(a) 

(b) 

(c) 

(d) 

wherein R may be independently none, hydrogen or a straight chain or branched C_1-C_8 alkyl group, optionally substituted by an alcohol, sulphate, sulphonate, halogen or amine, and R_1 may be independently hydrogen or a straight chain or branched C_1-C_8 alkyl group, optionally substituted by an alcohol, sulphate, sulphonate, halogen or amine.

3. Composition according to claim 2, wherein the water-soluble organic acid is selected from the group consisting of citric acid, acetic acid, propionic acid and succinic acid.

4. Composition according to claim 3, wherein the composition contains citric acid and another water-soluble organic acid selected from the group consisting of acetic acid, propionic acid and succinic acid.

5. Composition according to any of claims 1-4, wherein the composition contains at most 5% by weight of a sequestering agent.

6. Composition according to any of claims 1-5, wherein the sequestering agent is selected from the group consisting of polycarboxy derivatives of amines or polyamines, nitrilotriacetic acid, and phosphoric acids.

7. Composition according to any of claims 1-6, wherein the solid, substantially water-insoluble organic peroxy acid is a peroxycarboxylic acid derived from a dicarboxylic acid containing 8 to 13 carbon atoms.

8. Composition according to claim 7, wherein the organic peroxy acid is 1,12- diperoxy dodecane dioic acid.

9. Composition according to any of claims 1-7, further comprising up to 50% by weight of a surfactant selected from anionic surfactants, nonionic surfactants and mixtures thereof.

10. Aqueous disinfectant composition prepared by diluting the concentrated composition according to any of claims 1-9 to a working concentration of 0.1-5.0 % by weight in water, and having a pH in the range of from 2 to 6.

11. Disinfectant composition according to claim 10, wherein the composition has a pH in the range of from 3 to 5.

12. Process for disinfecting a surface or an article, wherein the aqueous disinfectant composition of claim 10 is applied.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 20 0974

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,A	EP-A-0 461 700 (AKZO N.V.)		A01N37/16 //(A01N37/16, 37:02, 37:04, 25:04)
A	EP-A-0 313 143 (UNILEVER N.V.)		
A	WO-A-9 103 590 (HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN)		
D,A	US-A-4 147 720 (FMC CORPORATION)		

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

A01N
A61L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19 AUGUST 1993	DONOVAN T.M.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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